A STUDY OF THE INTRODUCTION OF IONS INTO THE REGION OF STRONG FIELDS WITHIN A QUADRUPOLE MASS SPECTROMETER

By

WILSON M. BRUBAKER

BELL & HOWELL RESEARCH CENTER
360 SIERRA MADRE VILLA
PASADENA, CALIFORNIA

CONTRACT NASW-1298

SIXTH
QUARTERLY PROGRESS REPORT
for the period
17 NOVEMBER 1966 THROUGH 17 FEBRUARY 1967

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C.

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ABSTRACT

The work this quarter has been concerned primarily with the operation of the two quadrupoles with round and hyperbolic rods. These two units are operated in parallel, in a common atmosphere. The frequency of excitation has been lowered from 1.6 MHz to 1.0 MHz. Preliminary data show that at comparable sensitivities the resolving power of the hyperbolic quadrupole exceeds that of the round by a factor of two.

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INTRODUCTION

This report covers the work done by the Bell & Howell Research Center on NASA Contract NASW-1298 from 17 November 1966 through 17 February 1967. This is the sixth quarter of the Contract.

This project is concerned with the introduction of ions into the region of strong fields in the quadrupole mass filter, and with the comparison of the performances of quadrupole structures with round and with hyperbolic field-forming surfaces.

During this quarter preliminary data have been obtained from which the operation of quadrupoles with round and hyperbolic surfaces may be compared. A new ion source of simple design has been assembled and used briefly.

Abstracts have been submitted for papers to be given at the National Mass Spectrometry (ASTM Committee E-14) Meeting in Denver in May, and at the International Mass Spectrometry Conference in West Berlin in September. These abstracts appear in the appendix of this report.

ELECTRONIC APPARATUS

The apparatus for the control and excitation of the round and hyperbolic rod quadrupoles consists of several discrete sections which are depicted in Figure 1. Figure 2 shows a front view of the apparatus. All controls and information readout devices concerned with the actual data collection are readily accessible to the operator. The gas inlet system can be seen at the extreme right. The crystal oscillator, amplitude modulator, and rf power amplifer are located on a short rack section in the rear and are not shown. Essential details of each major section will be described later.

Design Goals

The principal goal is to provide an apparatus of sufficient refinement to enable a critical comparison to be made of the performance of the quadrupoles with round and with hyperbolic field-forming surfaces. In other words, the mass resolving power is not to be limited by the electronic components.

Since the scanning of one mass peak is accomplished in less than 30 seconds, the gradual changes in electrical parameters due to temperature changes, and/or component aging, become insignificant. Therefore the emphasis is placed on maximum stability during a comparatively short time.

A feeling for the permissible tolerances in the operating parameters of voltage and frequency is obtained by reference to the dimensionless variables a and q. Logarithmic differentiation of the defining equations for a and q relates variations in the above mentioned variables and the mass of the ion. In the apparatus under consideration the dc potentials are caused to be proportional to the ac potentials through the use of negative feedback amplifiers. This limits the motion of the working point to a line through the origin of the stability diagram. Under these conditions it is not necessary to consider separately the variations of the dc potentials. Differentiation of the defining equation for q yields

$$dq/q = dV_{ac}/V_{ac} - dm/m - 2\ dr_o/r_o - 2\ df/f$$

Assuming that dq is zero and limiting our attention to the electrical quantities,

$$dm/m = dV_{ac}/V_{ac} - 2\ df/f \qquad (1)$$

Experience has shown that if the sum of the possible variations of Equation (1) are less than about 1×10^{-4} the resolving power will not be limited significantly by these variations. Accordingly, such a goal is attempted in the design and assembly of this apparatus.

Crystal Oscillator

The crystal oscillator circuit is designed to operate at seven frequencies from 0.5 through 4.0 MHz. Crystals were selected so that the available frequencies differ by factors of $2^{1/2}$. The crystal oscillator frequency varies with temperature less than one part in 10^6 per degree Celsius which constitutes the major long-term drift. This section is electrostatically shielded from the other modules and is capacitance coupled to the grid of the modulator.

Amplitude Modulator and Power Amplifier

The constant amplitude rf voltage from the crystal oscillator is amplified by varying amounts to achieve the desired excitation levels for the quadrupoles. The level to which the rf voltage is amplified is determined by the dc scanning control voltage which, in turn, is regulated by negative feedback. The maximum power available from the plate tuned power amplifier is about 90 watts. Two plug-in rf transformers (tank coils) cover the entire frequency range. The output is link coupled to a 52 ohm coaxial transmission line. Since the transmission loss at 4 MHz is only 0.4 db per 100 ft., the location of the quadrupole is of little importance.

Quadrupole Excitation Tank Coil

A second plug-in rf transformer (tank coil) is located in the immediate vicinity of the quadrupoles (See Figure 3). Its function is to provide the necessary impedance match between the transmission line and the resonant circuit of which the rod and segment capacitances are a major part. Four of these plug-in coils cover the entire range of frequencies. Corresponding electrode terminals of each quadrupole are connected in parallel so that the same dc and ac potentials are simultaneously applied to both.

High Frequency Rectifiers

Two independent dc feedback voltages for the control unit are produced by two full wave shunt rectifiers capacitance coupled to the tank coil. One controls the modulator to keep the ac potential stable and proportional to the scanning control voltage. The other is used as a reference for stabilizing the dc/ac ratio. In each case the negative feedback voltage is compared with its respective control voltage at the input of a high gain operational amplifier. The open loop gain of these stabilizing circuits is sufficient to enable these portions of the apparatus to achieve the design goals.

Conclusions

The new apparatus has been in operation for several months during which time data have been collected with both quadrupoles operating with their corresponding electrodes in parallel. With the exception of a few typical defective components and loose connections, during the debugging phase, the design goals have been met. It appears evident that the refinements in voltage and frequency stability have kept the electronic apparatus from limiting the resolving power of the quadrupoles.

EXPERIMENTAL PROCEDURE

General

Throughout the design of the apparatus consideration was given to the duplicity of equipment and the correspondence of operating parameters in order to concentrate on the difference in performance between the round and the hyperbolic field-forming surfaces in the quadrupole. To this end, two quadrupoles that differ only in the shape of the rods were mounted side by side on a common vacuum system as is seen in Figure 3. Both quadrupoles respond to ions generated from a common atmosphere which is monitored by a Bayard-Alpert ionization gauge and by a 3" quadrupole responsive to the krypton pressure. These pressure sensors are placed symmetrically with respect to the two quadrupoles. In addition to the above considerations the quadrupole assemblies are mechanically identical so that the ion sources, rods, and secondary emission multipliers are completely interchangeable.

By means of a simple servo system comprising an ion pump operating at reduced voltage, a strip chart recorder with a retransmitting slidewire, an ac amplifier, and the 3" quadrupole which is responsive to krypton, the partial pressure of krypton is stabilized. The partial pressure of mass 84 krypton isotope during these experiments was about 5×10^{-8} torr.

All potentials affecting the ion energy are common to both ion sources. Focusing potentials are individually adjusted for optimum performance. Thus the ion beams entering the quadrupoles are quite similar. The excitation of the two quadrupoles is identical since corresponding rod and segment terminals are electrically connected together.

Detection of the transmitted ions is aided by secondary emission multipliers supplied from a common high voltage power supply. Identical electrometer amplifiers are used to drive pen and ink recorders. Otherwise, the outputs of the multipliers are connected directly to an oscilloscope.

Data Collection

The procedure used in collecting data is as follows: (1) The partial pressure of krypton is adjusted to a point where it is stable. (2) The width of the scanned spectrum is adjusted to include only mass peaks 83 and 84. (3) The scanning rate is adjusted to about 10 scans per second. This is slow enough for faithful display of the peak shape and fast enough for viewing and for photography with a one-second exposure. (4) The vertical sensitivity of the cathode ray oscilloscope is adjusted so that the maximum peak height at the point where peak height becomes independent of decreasing dc/ac ratio is the useful limit of the screen. (5) Photographs are then made at step changes in dc/ac ratio from which a family of curves is derived showing peak height as a function of resolving power. (6) The above procedure is then repeated for the other quadrupole.

Data Reduction

Measurements of peak separation, height, and width at 10% of peak height are made from the photographs with the aid of a decimal scale. These data are normalized to the current observed when the peak height becomes independent of the decreasing dc/ac ratio. This appears to be 100% transmission in that the peak height is independent of the resolving power. This normalization is done in order to eliminate the influence of variations in the ion sources and the secondary emission multipliers.

EXPERIMENTAL DATA, ROUND AND HYPERBOLIC QUADRUPOLES

Preliminary data have been obtained on comparative studies of the performance of round and hyperbolic quadrupoles. The initial data indicate a dramatic difference in the two units. At comparable sensitivities, the resolving power of the hyperbolic quadrupole exceeds that of the round by a factor greater than two! In order to assure that this difference is in reality due to the shape of the rods, and not to any other cause, the units were disassembled and the rods interchanged. All other components (sources, secondary emission detectors) remained as before. It was gratifying to find that the data after the interchange were essentially unchanged. This gives us confidence that the observed differences are in fact due to the contours of the field-forming surfaces.

The preliminary data are presented in Figures 4 and 5. These data were obtained through the use of the multipliers and an oscilloscope. The ion currents are normalized to the current observed at low resolving power where the peak height is independent of resolution. This is different from the normalization used in previous data. The change was made because the gain of the multiplier appears to vary with the position of the incident ion beam. This variability is most apparent when the height of the mass 84 peak of krypton is compared to the total ion current obtained by reducing the dc component of the rod potentials to zero. The observed total ion current is considerably smaller than the sum of the resolved peaks! In the total ion current mode of operation the ions are concentrated near the axis of the device, and strike the multiplier in a small area near the center. The multiplier gain seems to be lower than average in this vicinity. With this normalization method, these data appear to be independent of this variability of gain as a function of position in the multiplier.

Because the two quadrupoles are excited simultaneously from a single oscillator supply, the capacitance load is much higher. Consequently the oscillator power available is insufficient to excite the two quadrupoles at the 1.6 MHz used in the experiments of the previous quarter. Therefore 1.0 MHz was selected for these experiments.

INTERPRETATION OF EXPERIMENTAL DATA

Experiment indicates that the resolving power capability of the hyperbolic quadrupole is twice that of the round when all other conditions are as similar as they can be made. Theory [1] relates resolving power directly to the excitation potential. This suggests that a hyperbolic quadrupole will have a resolving power equivalent to that of a round one when the excitation potential of the hyperbolic is only half that of the round! This represents a power savings of 75%!

If the instrument radius, r_0, for the hyperbolic quadrupole is made 70% as large as it is for the round quadrupole, the operation of the two instruments at the same frequency produces the same fields when the potential applied to the hyperbolic is half that applied to the round. The preliminary data indicate that the resolving power of the two instruments would be expected to be the same.

The predicted savings in both power and mass which results from the use of hyperbolic rod contours is of paramount importance for space applications, and probably warrants the additional cost of the hyperbolic structure.

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[1] Brubaker, Wilson M., Study and Development of the Paul-Type Mass Spectrometer. Contract # AF 19(604)-5911, Final Report, p. 16, Eq. 39.

ION SOURCE DEVELOPMENT

The ion source used previously was designed for use with a conventional quadrupole, in which it is necessary for the ions to be injected near the instrument axis. The advent of the delayed dc ramp mode of operation permits the transmission of ions which enter farther from the axis. Since the old source could not be made to produce an ion beam of large diameter, a new one was designed and built. The dimensions of the new source provide an aperture whose diameter is half that of the rods. The optimum aperture size is most probably smaller than this, but in order to demonstrate this circumstance, a large aperture must be provided. Its dimension is readily reduced by the addition of a mask.

The new ion source design takes advantage of the experience gained with the old one. In the former one, shown in Figure 6, the potentials of the electrodes were adjustable. It was found that optimum operation was obtained when the potentials on most of the electrodes which enclose the ionizing region are quite similar. Hence, in the new design, Figure 7, the outer periphery of the ionizing region is made of a wire mesh screen of high transparency, forming a uni-potential surface. As in the earlier source, the ionizing electrons converge toward the axis of the instrument, making their density a maximum in the vicinity of the axis.

The gradient which urges the ions toward the quadrupole is provided by leakage fields from the ends. The field at the end remote from the quadrupole results from a small potential on the repeller. The field at the exit end of the quadrupole results from a larger (negative) potential placed on the ion focusing electrode. The combination of these two fields provides the necessary gradient to direct the ions into the quadrupole.

Since the ions are formed in the cylinder which is uni-potential, it is anticipated that the energy of the emerging ions will be more homogeneous than in the previous source. This is of increasing importance when the energy of the ions is lowered as it is in the delayed dc ramp mode of operation.

ION SOURCE DATA

Preliminary data with the new source have been obtained using a four-volt ion accelerating potential. Two aperture sizes have been used, namely 0.100 and 0.300 inches. The sensitivity as a function of the resolving power for each aperture is shown in Figure 8. For comparison, the data obtained last quarter with the old ion source with a 0.030-inch aperture are repeated on the same scale.

Note first the sensitivity of the device with the 100-mil aperture. At resolving powers above 200 its sensitivity is about three times that of the old source, with 30-mil aperture. At resolving powers below 200 the advantage of the new source becomes greater.

The performance of the instrument with the 300-mil aperture is outstanding at the lower resolving powers. However, the sensitivity falls rapidly with increasing resolving power. For resolving powers above about 300 the sensitivity is less than with either of the other two.

While the performance of the new ion source is better than that of the old source at the higher resolving powers, it is comparable to the performance which is obtainable with the old source if optimum potentials are provided for all electrodes. One of the main advantages of the new ion source is the ease with which it is adjusted. The potential adjustments are non-critical in the new source; in the old one a number of the potentials must be adjusted critically for optimum performance.

CONCLUSIONS

Findings of preliminary experiments with round and hyperbolic rod quadrupoles are most encouraging. They indicate that a quadrupole of a given performance will operate at much lower excitation power if the field-forming surfaces are hyperbolic, instead of round. For space missions this saving of power more than offsets the additional cost of fabricating the hyperbolic rods.

NEXT QUARTER'S ACTIVITIES

During the next quarter, additional data will be obtained which compare the performance of the two quadrupoles (with round and hyperbolic rods). The data will be extended to include the conventional mode of operation as well as the delayed dc mode which has been used in the preliminary investigations. The apparatus will be operated at different excitation frequencies. These data will give further indication of the savings in power which may be achieved through the use of hyperbolic instead of round rods.

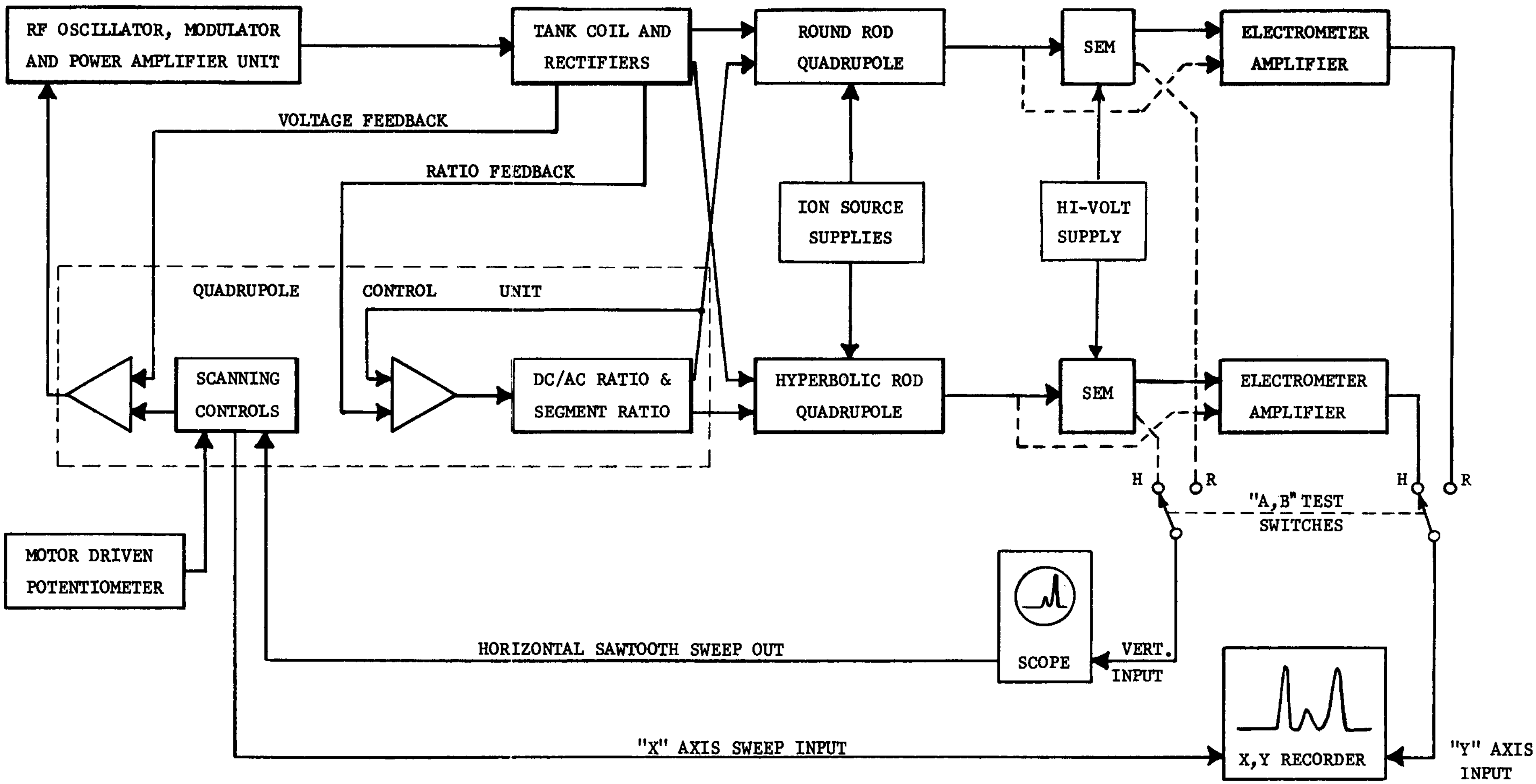

FIGURE 1.

BLOCK DIAGRAM OF ELECTRONIC APPARATUS

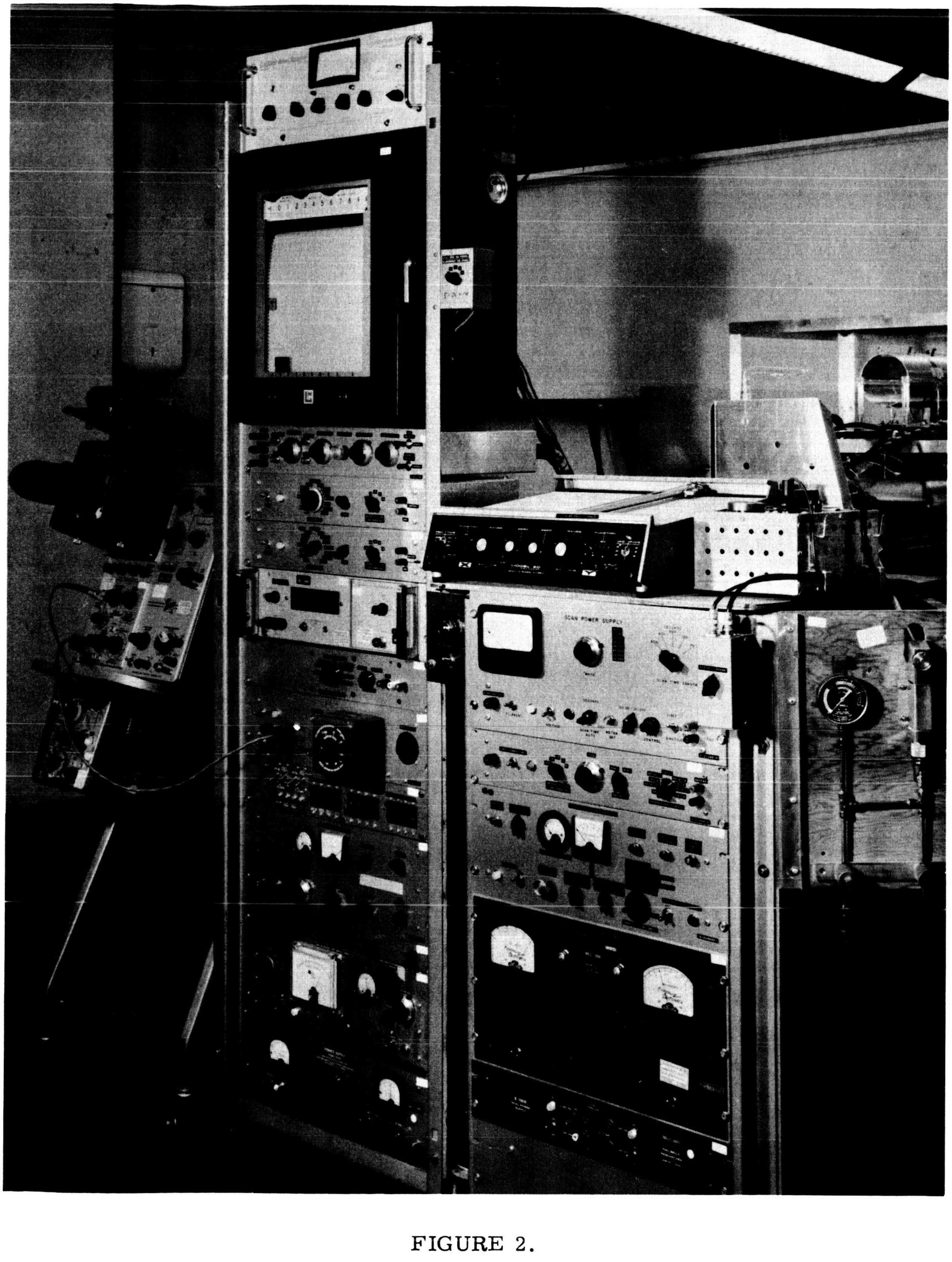

FIGURE 2.

ELECTRONIC APPARATUS

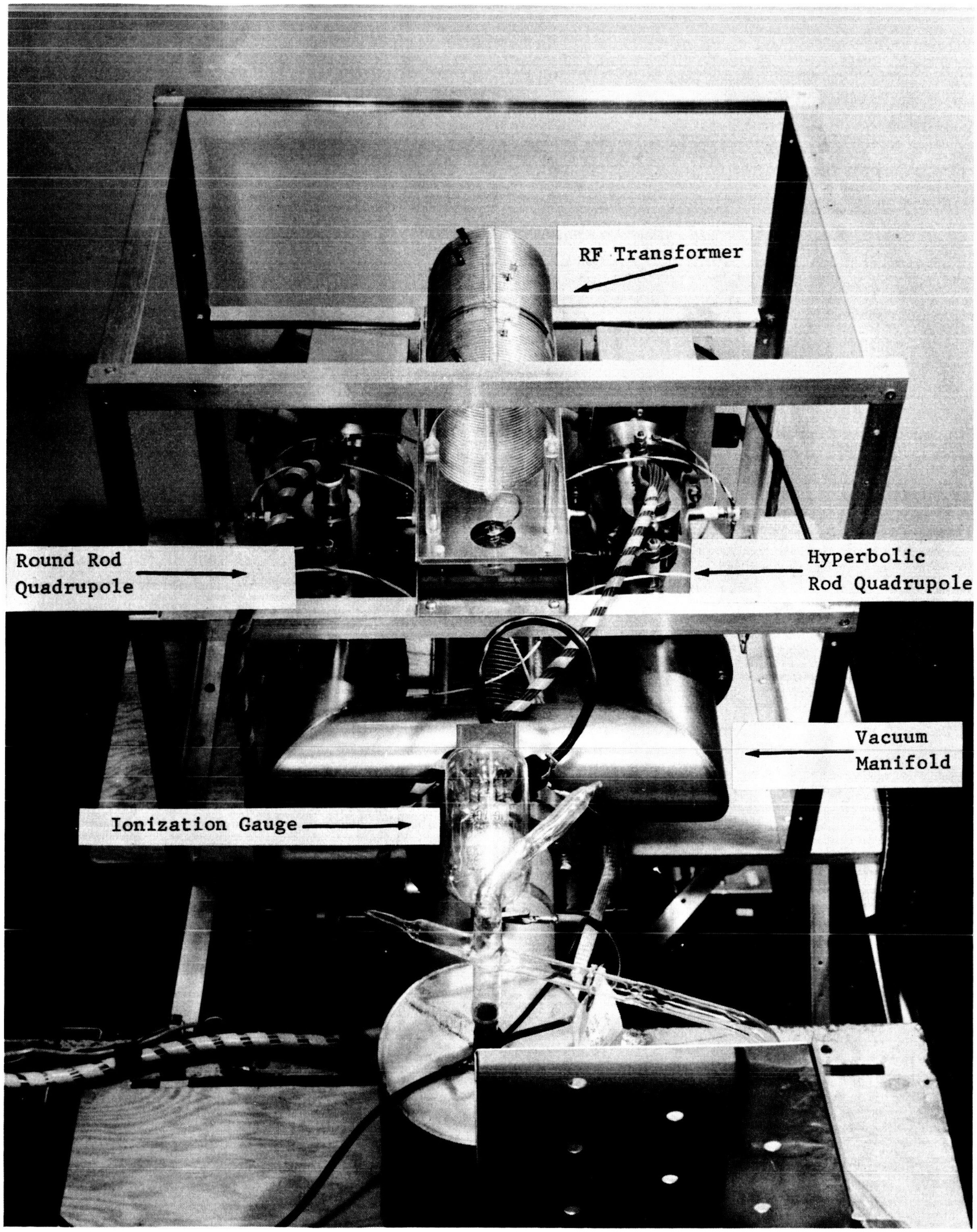

FIGURE 3.

VACUUM MANIFOLD ASSEMBLY

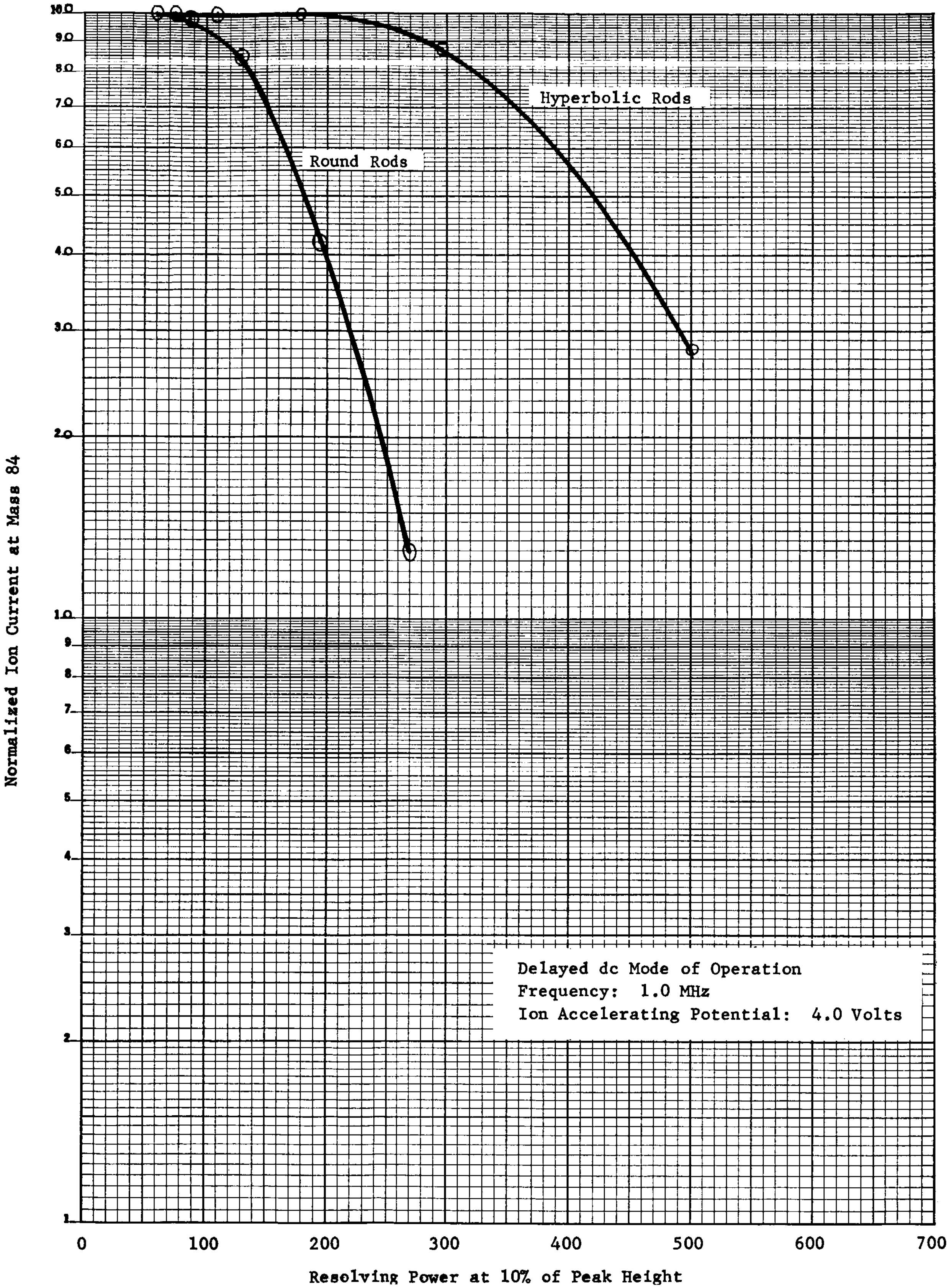

FIGURE 4.

COMPARISON OF PERFORMANCE CHARACTERISTICS
OF ROUND AND HYPERBOLIC ROD QUADRUPOLES

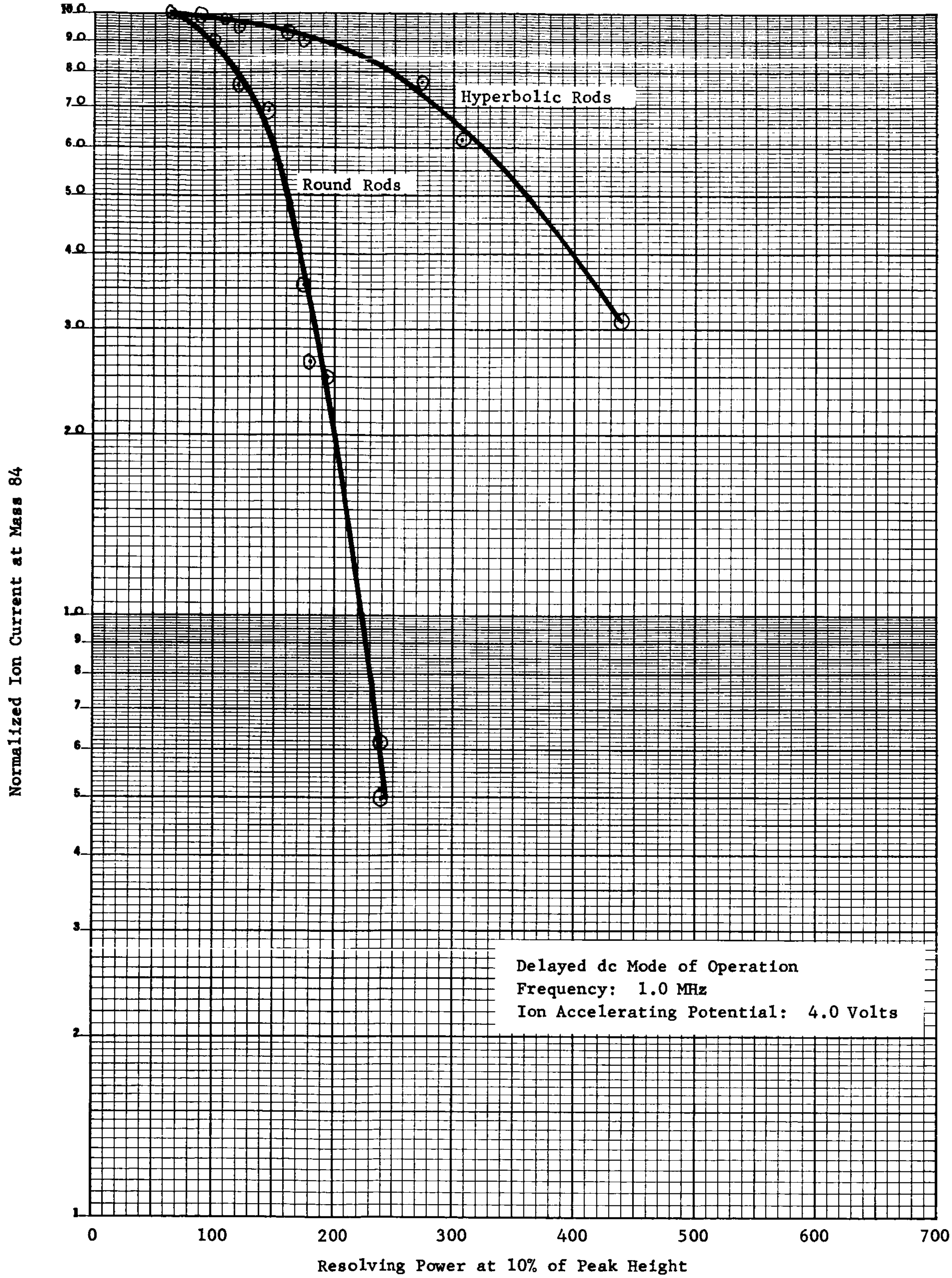

FIGURE 5.

COMPARISON OF PERFORMANCE CHARACTERISTICS
OF ROUND AND HYPERBOLIC ROD QUADRUPOLES
AFTER THE RODS WERE INTERCHANGED

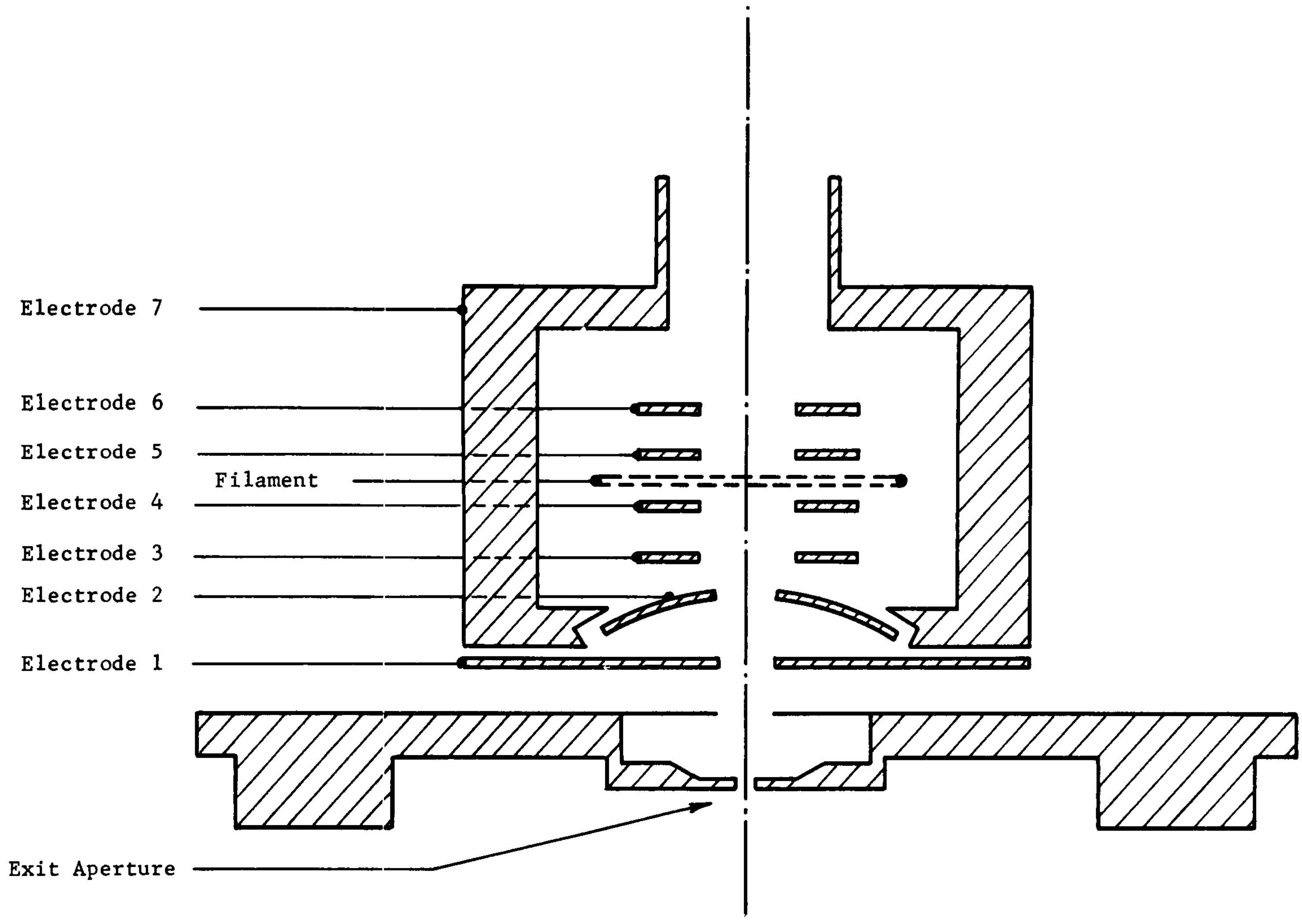

FIGURE 6.

GEOMETRY OF OLD ION SOURCE

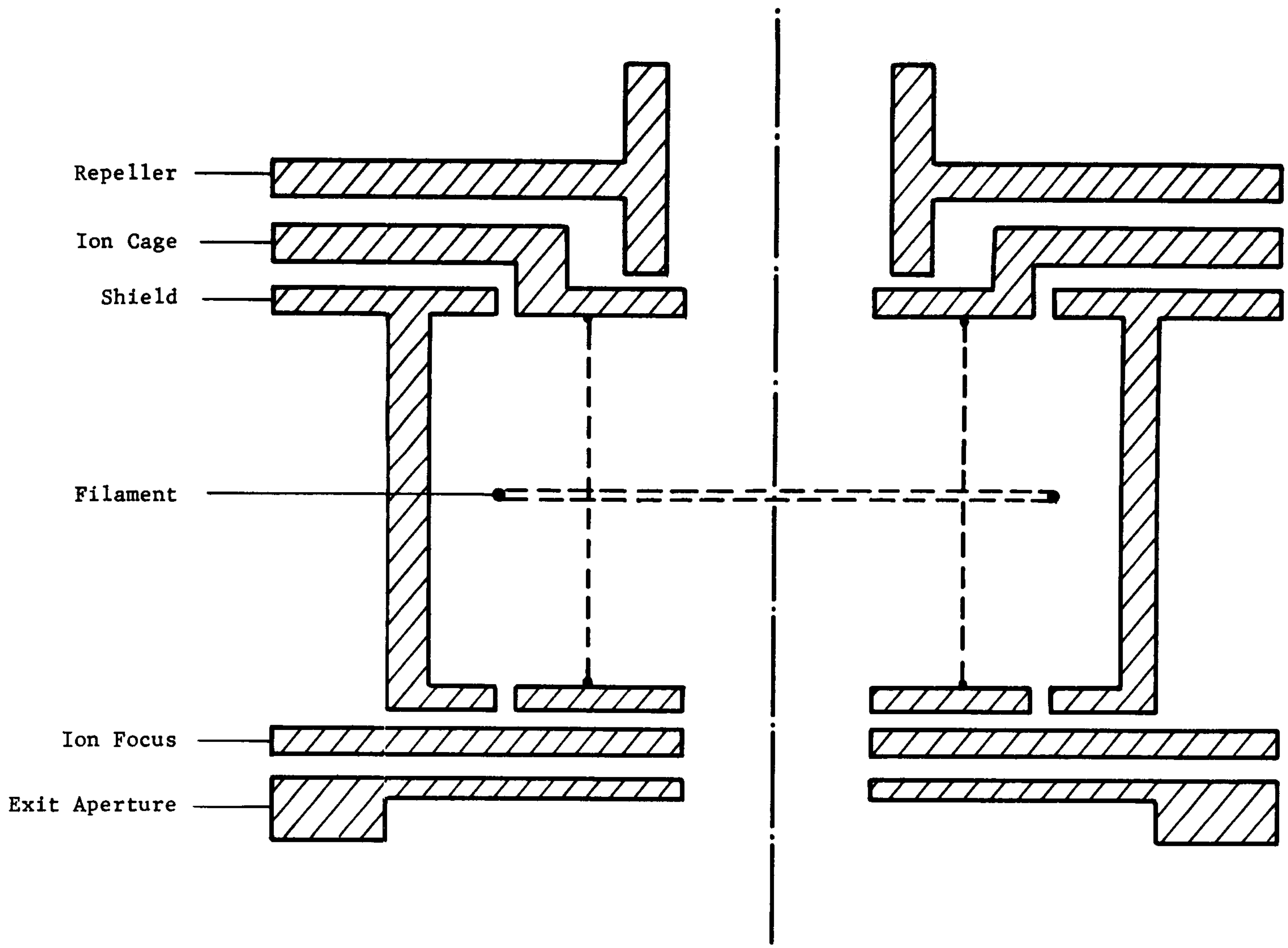

FIGURE 7.

GEOMETRY OF NEW ION SOURCE

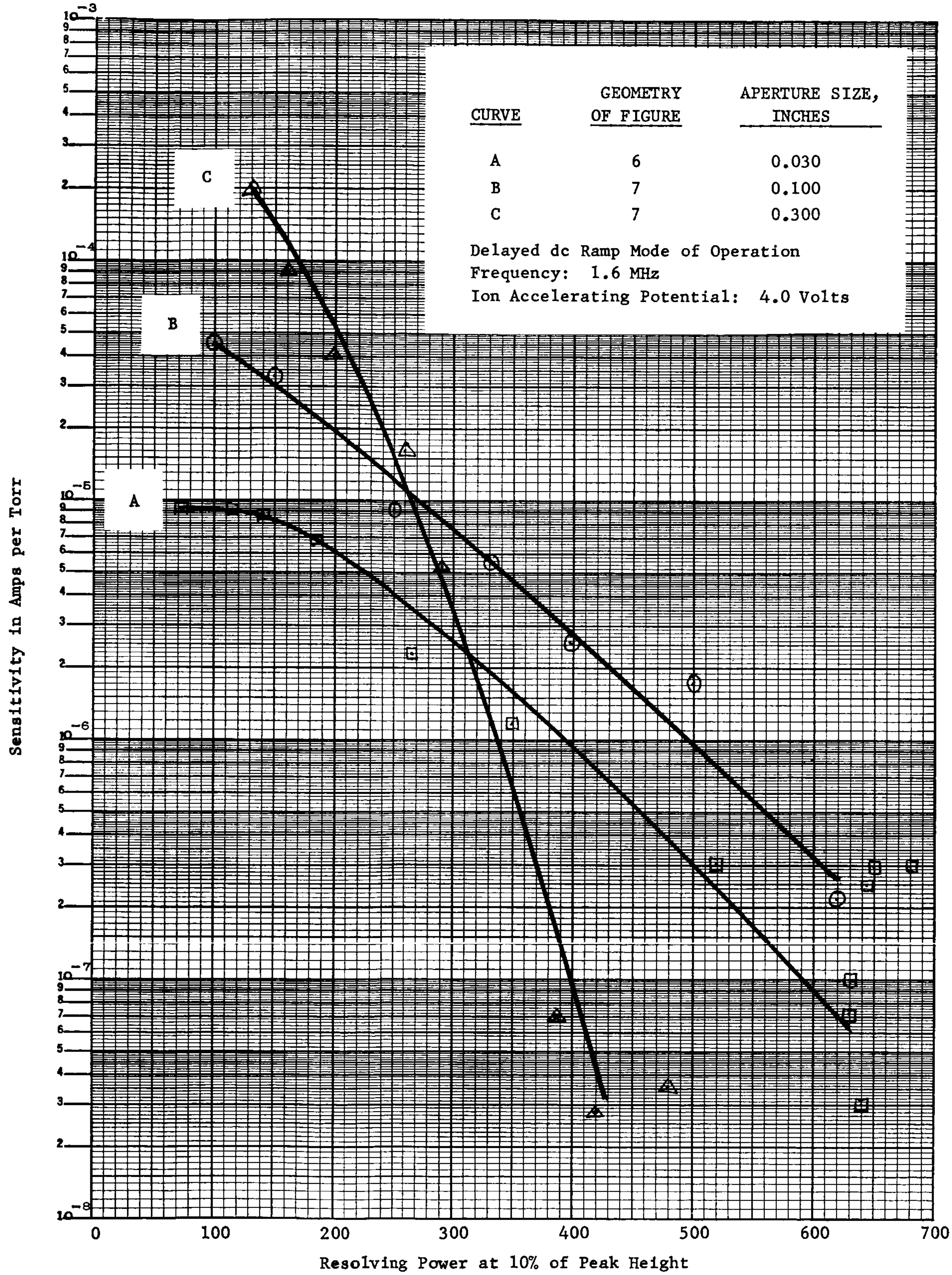

FIGURE 8.

OPERATING CHARACTERISTICS OF QUADRUPOLE
WITH DIFFERENT ION SOURCE CONFIGURATIONS

APPENDIX

Abstract of Paper to be Presented at the
Fifteenth Annual Conference on Mass Spectrometry and Allied Topics
in Denver, May 14-19, 1967

THE EFFICIENT INTRODUCTION OF IONS INTO A QUADRUPOLE MASS FILTER[1]

Wilson M. Brubaker

Bell & Howell Research Center
Pasadena, California

The efficiency with which ions are introduced into a quadrupole mass filter is increased by several powers of ten by the appropriate control of the fields at the entrance to the filter. This is accomplished by using an additional set of four electrodes. The potentials applied to these additional electrodes have a smaller ratio of dc to ac values than the potentials applied to the quadrupole. Computer studies reveal the high vulnerability of the entering ions to the impulses which they receive as they traverse the fringe fields of the conventional quadrupole. Further studies with the computer reveal the effectiveness of the altered fields in eliminating these undesired impulses. Experimental data compare the operation of the quadrupole with and without use of the additional electrodes. It is found that the sensitivity of the instrument can be increased by powers of ten without degrading the resolving power through the use of these auxiliary electrodes.

[1]This research was supported in whole or in part by the National Aeronautics and Space Administration under Contract No. NASW-1298.

Abstract of Paper to be Presented at the
International Mass Spectrometry Conference in Berlin
September 25-29, 1967

IMPROVED QUADRUPOLE[1]

Wilson M. Brubaker

Bell & Howell Research Center
Pasadena, California

Experimental data reveal that the sensitivity of the conventional quadrupole can be increased by a factor of ten to one-hundred with no sacrifice in the resolving power. This is accomplished through the use of a set of four additional electrodes at the ion entrance end of the mass filter. As an ion traverses the fringe fields of a conventional quadrupole the working point moves through the y-unstable portion of the stability diagram. Under these circumstances, computer studies have shown that the ion receives a large impulse in the y-direction. By appropriately energizing the auxiliary electrodes of the improved quadrupole, it is possible to have the working point remain within the x- and y-stable portion, and thus to avoid the undesirable radial impulse. The results of computer studies and experimental data are presented.

[1]This research was supported in whole or in part by the National Aeronautics and Space Administration under Contract No. NASW-1298, monitored by Dr. Donald P. Easter.